THE SYNTHESIS OF HINDERED SYMMETRICAL DI-ARYLOLEFINS AND *ORTHO*-TERPHENYLS

BY

WILLIAM DEAN FRASER

S.B., Harvard University, 1938

M.S., University of Illinois, 1939

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1941

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ACKNOWLEDGMENT

The author wishes to take this opportunity to express his sincere appreciation to Professor Roger Adams for his help, advice and encouragement during the past three years of graduate study.

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INTRODUCTION

Symmetrical di-arylolefins with two points of restricted rotation are theoretically available by various 1,4 additions to properly substituted 2,3-diarylbutadienes, and hindered *ortho*-terphenyls could apparently be prepared by a Diels-Alder reaction between the same butadienes and the customary addends. The most likely method for the preparation of such dienes is by the dehydration of the pinacols of methyl aryl ketones. The object of this research, therefore, was to explore the possibilities of these syntheses with the ultimate aim of producing hindered compounds suitable for the demonstration of the stereoisomeric properties which such molecules should possess.

DISCUSSION OF RESULTS

A literature survey of over one hundred and fifty pinacols of all types indicated that the most promising synthesis of the desired symmetrical di-methyl di-aryl glycols was by the electrolytic reduction of the corresponding methyl aryl ketones. Using the customary procedure as described by Swann [1], the reduction was shown to be successful for making acetophenonepinacol, aceto-*m*-xylenepinacol, acetomesitylenepinacol and aceto-tri-ethylbenzenepinacol. The reduction of *p*-phenylacetophenone, aceto-*i*-durene and propiophenone also gave the pinacols but in too small yield under these conditions to be synthetically useful. No pinacol was isolated from the reduction of acetobromomesitylene or aceto-tri-*i*-propylbenzene by this procedure.

Dehydration of acetophenonepinacol by an adaptation of the methods of Stern [2] and Johlin [3] proved to be practical for the preparation of diphenylbutadiene. Similarly dimesitylbutadiene was obtained in very satisfactory yield by treatment of the pinacol with acetyl chloride and acetic acid in benzene solution. Since a thorough study of the reactions of diphenylbutadiene by Allen, Eliot and Bell [4] was published while this research was in progress, attention was concentrated more on the mesitylene compound. The dehydration of the other hindered pinacols was not attempted principally because the resinous nature of the reduction product made them less satisfactory to handle.

The 1,4 reduction of 2,3-dimesitylbutadiene gave a compound apparently identical with the product from 1,4 addition of hydrogen bromide to the same diene followed by removal of the bromine by reduction with zinc and acetic acid. Another attempt to make the same butene by 1,4 addition of bromine followed by reduction gave none of the desired product but regenerated the diene in quantitative yield. Bromination of the butene gave on the first attempt two compounds which were separated only with difficulty and which proved to contain one and two bromines respectively. Further bromination of the 1,4 bromine addition product led to a mixture which was abandoned because the fractions gave no true melting points. Thus the eventual goal of this part of the research, the proof of the existence of diastereoisomers of 2,3-di-(bromomesityl)-butene-2, has not been reached, though uncompleted work tends to show that such forms do exist.

The Diels-Alder condensation of diphenylbutadiene with maleic anhydride was quite successful, leading to an adduct previously characterized by Allen, Eliot and Bell.[4] Condensation with ethyl acrylate also gave the expected tetrahydrobenzoic ester, and this compound was easily dehydrogenated and hydrolyzed to 3,4-diphenylbenzoic acid, also made by Allen, Eliot and Bell, though by a slightly different method. The corresponding reactions with dimesitylbutadiene led to analogous products only at high temperatures, 200° for the maleic anhydride addition and 200-250° for the corresponding reaction with ethyl acrylate.

SUMMARY

The projected syntheses of hindered, symmetrical di-arylolefins and *ortho*-terphenyls have been shown to be practicable. One example of each synthesis has been carried to completion, and a group of pinacols has been made suitable for the preparation of a series of compounds to demonstrate the predicted stereoisomeric forms. Thus bromination of either the *cis* or *trans* 2,3-dimesitylbutene-2 would give 2,3-di-(bromomesityl)-butene-2 which is a hindered, symmetrical di-arylolefin with two points of restricted rotation and which should exist in a dissymmetrical *dl* form and a *meso* form with a center of symmetry in the *trans* or a plane of symmetry in the *cis* configuration. Quite similarly, bromination of 3,4-dimesitylbenzoic acid should give a hindered *ortho*-terphenyl with two points of restricted rotation capable of existing in two *dl* modi-

fications. Bromination of 4,5-dimesitylphthalic acid would likewise give a hindered, symmetrical *ortho*-terphenyl which should have a dissymmetrical racemic form and a *meso* form with a plane of symmetry between the carboxyls.

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VITA

The writer was born in Wells River, Vermont, on October 3, 1916. His education throughout grammar school and the first two years of high school, however, was in the public schools of Rochester, New Hampshire, where he lived between the ages of six and fifteen. He then attended Phillips Exeter Academy for three years and was graduated in June of 1934. Four years of undergraduate work at Harvard University were completed in June of 1938, and he entered the University of Illinois Graduate School in the following September. He received the degree of Master of Science from the University of Illinois in June of 1939 and was a research assistant for Professor Roger Adams during the academic year 1940-1941.

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